OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-95-1-0551

PR Number 96PR01007

Title of GRANT or CONTRACT

Development and Application of In-Situ, Real Time and Ex-Situ Characterization Techniques to Study the Growth of High Temperature Superconducting (HTSC) Films and Interfaces

Name(s) of Principal Investigators: Eugene A. Irene
(Co-P.I.'s O. Auciello, A.R. Krauss and G.E. McGuire)

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Date Submitted: June 27, 1997

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Principal Investigator: Eugene A. Irene (Co-P.I.'s O. Auciello, A.R. Krauss and G.E. McGuire)

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http address: None yet. In progress.

a. Number of papers submitted to refereed journals, but not published: _4___
b. + Number of papers published in refereed journals (for each, provide a complete citation): _1___
c. + Number of books or chapters submitted, but not yet published: _0___
d. + Number of books or chapters published (for each, provide a complete citation): _1___
e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): __0__
f. Number of patents filed: __0__
g. + Number of patents granted (for each, provide a complete citation): __0__
h. + Number of invited presentations (for each, provide a complete citation): _5___
i. + Number of submitted presentations (for each, provide a complete citation):__0__
j. + Honors/Awards/Prizes for contract/grant employees (list attached): _1___
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
E.A. Irene Elected to "Fellow" of American Vacuum Society, June 1997

k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: __3__

Graduate Students: _2___

Post-Doctoral Associates: __1__

including the number of,

Female Graduate Students: _1___

Female Post-Doctoral Associates: _0___

Minority* Graduate Students: _0___

Minority* Post-Doctoral Associates: __0__

Asian Graduate Students: _1___

Asian Post-Doctoral Associates: __0__

l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

Office of Naval Research: Oct 1991-April 1997, $355K, "Passivation of Semiconductor Surfaces"

National Science Foundation Engineering Center at North Carolina State University, Subcontract, Oct 1996-Sept 1997, $150K, "Part I: Ultra Thin Film Characterization Methodologies and Part II: An In-Situ During Process Study of Selective Deposition of Silicon Based Thin Films"

National Science Foundation: Jan.1 1997- Dec 31 1999, $298K "Thin Film Growth and Deposition Studies Under Energetic Conditions: Ion Beams and Electron Cyclotron Resonance Plasmas"

Defense University Research Instrumentation Program Award (ONR), June 1996-Sept.1997 $321K, "In-Situ Real Time Film Processing and Analysis System for High Temperature Superconductor Films"

All of these projects are involved with ultra thin films, film growth and interfaces. Thus there is considerable cross-fertilization in terms of techniques and methodology, particularly with in-situ real time ellipsometry. However, the present ONR-NSF program deals with superconductor films and interfaces and the other projects deal with semiconductor surfaces and dielectric films. Thus, the materials systems are decidedly different. The exception above is the DURIP grant which is directly applicable to the present ONR grant and enable the construction of a world-wide unique process and characterization system primarily aimed at HTSC films but generally suited for any complex oxide films.

a. Papers submitted to refereed journals, but not published:

"An In Situ Ellipsometry Study of Oxygen Diffusion In and Out of $YBa_2Cu_3O_{7-\delta}$ Thin Films," by A. Michaelis, E.A. Irene, O. Auciello, and A.R. Krauss, J. Appl. Phys. (in press, 1997).

"Effects of Water on Diffusion of O and Corrosion of $Yba_2Cu_3O_{7-x}$ Thin Films," by A. Michaelis, E.A. Irene, O. Auciello, and A.R. Krauss, J. Appl. Phys. (in press, 1997).

"Studies of Ferroelectric Film Growth Processes Using In Situ, Real-Time Ion Beam Analysis," by A.R. Krauss, O. Auciello, J. Im, V. Smentkowski, D.M. Gruen, E. A. Irene, and R.P.H. Chang, Integrated Ferroelectrics (in press, 1997). Invited Paper.

"Study of Growth Processes in Ferroelectric Films and Layered Heterostructures via In situ, Real-time Ion Beam Analysis," by O. Auciello, A. R. Krauss, and J. Im, in "Thin Film Ferroelectric Materials and Devices," R. Ramesh (Ed.), Kluwer Academic Publishers, The Netherlands (in press, 1997).

b. Papers published in refereed journals (for each, provide a complete citation):

"Studies of Film Growth Processes and Structural Determination of Ferroelectric Memory-Compatible $SrBi_2Ta_2O_9$ Layered Peroskite Surfaces via In-Situ Real Time Ion Beam Analysis", O. Auciello, A.R. Krauss, J. Im, D.M. Gruen, E.A. Irene, R.P.H. Chang and G.E. McGuire, Appl. Phys. Lett. 69, 2671 (1996).

d. Books or chapters published (for each, provide a complete citation):

"Sputter-Deposition of Ferroelectric Films and Layered Heterostructures: Analysis of Orientation-Microstructure-Property Relationships and In Situ, Real-Time Characterization of Growth Processes," by O. Auciello, A.R. Krauss, and K.D. Gifford, in "Ferroelectric Thin Films: Synthesis and Basic Properties," C.A. Paz de Araujo, J.F. Scott, and G.W. Taylor (Eds.), Gordon and Breach Publishers (1996) p.393-426.

h. Invited presentations (for each, provide a complete citation):

Electrochemical Society Montreal Canada, May 1997, "Ultra Thin Dielectric Film Characterization Studies", E.A. Irene

Corrosion Gordon Conference, New Hampshire, July 1997, " New Results in Silicon Oxidation - The Ultra Thin Film Regime", E.A. Irene

Sandia Laboratories, New Mexico, Jan 1997, " Thin SiO_2 Films for Gate Dieletrics", E.A. Irene

1996 North Carolina Materials Research Society Symposium, Research Triangle Park, NC, December 1996, "In Situ, Real-Time Characterization of High Temperature Superconducting and Ferroelectric Thin Film Growth Processes via Time-of-Flight Ion Scattering and Recoil Spectroscopy," by O. Auciello, A.R. Krauss, E.A. Irene, J. Im, and D.M. Gruen

9th International Symposium on Integrated Ferroelectrics, March 1-4, 1997, Santa Fe, New Mexico, "Studies of Ferroelectric Film Growth Processes Using In Situ, Real-Time Ion Beam Analysis," by A.R. Krauss, O. Auciello, J. Im, V. Smentkowski, D.M. Gruen, E. A. Irene, and R.P.H. Chang.

EOY Report - PART II

a. Principal Investigator: Eugene A. Irene (Co-P.I.'s O. Auciello, A.R. Krauss and G.E. McGuire)

b. Current telephone number: (919)-966-1652

c. Cognizant ONR Program Officer: Dr. John Pazik

d. Program objectives:

1. Demonstrate Time-of-Flight Ion Scattering and Recoil (ToF-ISARS) Spectroscopy and Spectroscopic Ellipsometry (SE) for in-situ and real time characterization of HTSC thin films and processes.
2. Study HTSC thin film processes and interface reactions.

e. Significant results during last year (100-200 words) - be specific and comment on impact

Previously we have prepared 123 films on MgO using ion beam sputtering with T_c's of about 85K and we have shown that our material has the same spectroscopic ellispometric (SE) spectrum as appears in the literature and measured the orientation and composition using ToF-ISARS.

In the past year we have used the O sensitive 4 eV SE spectral region in order to perform in-situ real time annealing and corrosion studies on our 123 HTSC films. It is well known that the O content virtually dictates the Tc quality of the material. We have discovered that O diffuses in and out of 123 HTSC films via different mechanisms. In-diffusion of O is via a grain boundary mechanism, and is thickness independent while out-diffusion is via a bulk diffusion mechanism. Additionally, H_2O in the annealing ambient greatly enhances the out-diffusion but hardly affects the in-diffusion. Increased H_2O yields corrosion which was followed in-situ and in real time. Finally, we have measured the anisotropic dielectric function for single crystals and HTSC films which will provide useful new data from which to study the material.

In summary we have demonstrated in-situ ellipsometry as a sensitive tool for studying HTSC and other complex oxide film formation and properties. This work combined with our earlier work establishing ToF-ISARS as a powerful tool complementary to SE, completes one main objective of the research. Much of the effort this year with the award of a DURIP has been the design and construction of a combined process and analysis system containing ion sputter deposition with SE and ToF-ISARS. This system will be a world-wide unique facility. All major subsystems have been ordered and we await arrival of about 30% of the hardware. We estimate a Jan 1 commencement of experiments in the new system.

f. Brief (100-200 words) summary of plans for next years work

The first objective is to complete the unique in-situ real time process and analysis system containing ion sputter deposition with SE and ToF-ISARS. Once complete in-situ real time film deposition studies will commence. The first scientific objective is to correlate

the optical spectra (obtained via SE) of O in 123 HTSC films with the atomic position of O obtained from Angle Resolved Ion Scattering Spectroscopy (ARISS), and this will be complemented with T_c measurements. The O position and concentration is crucial in determining Tc in HTSC materials. The successful annealing studies will be continued in order to establish the corrosion mechanism in real time. Then we will explore the process parameter space in order to optimize 123 thin film preparation. All the experiments are planned for the new combined deposition and analysis system.

g. List of names of graduate students and post-doctoral(s) currently (during the report period) working on the project:

Dr. Alexander Michaelis (not paid from grant) returned to Germany in Feb 1997 and Mr. Imran Aftab left UNC with a M.S. in June 1997. Presently Ms. Ying Gao is a graduate student working on the project and 1/2 Post Doctoral will be added in Sept. 1997 (Dr. Pavel Bulkin).

EOY Report - PART III

Using separate facilities at UNC and Argonne National Laboratory we have demonstrated the in-situ and real time capability of spectroscopic ellipsometry (SE) and time of flight ion scattering and recoil spectrometry (ToF-ISARS) in studying thin films of 123 HTSC films. This was/is a major objective of the research. The 5-Part viewgraph (Figure 1) displays our ultimate objective of a world-wide unique combined ellipsometry-ToF-ISARS-deposition system for in-situ real-time process studies which is now funded via a DURIP. Based on our experimental results we have designed the system and commenced construction in June 1996. We will finish the hardware construction by September 1997 and anticipate full experimental capability by Jan 1, 1998. Tof-ISARS can perform atomic analysis, structure determination and defect analysis. SE can follow the evolution of film formation from nucleation through coalescence to growth. Combined, these two techniques can perform complete materials and process characterization in real time.

The major experimental results this year resulted from in-situ real time ellipsometry studies of the O diffusion in and out of 123 HTSC films in dry O_2 and vacuum ambients and with H_2O in the ambient. Figures 2 and 3 give an example of the in-situ real time SE data and analysis in terms of optical spectra. Figure 2 shows a summary of one of many annealing experiments of a YBCO film reported in terms of the actual ellispsometry measurables (Δ and Ψ) versus time of anneal at a single incident photon energy (4 eV). The Temperature history is also superimposed on the data. In reading this Figure time progresses from left to right. The first anneal was in vacuum and both Δ and Ψ increase albeit at different rates. At about 773K a change has occurred. The sample is then cooled to RT but the optical change persists. Then the anneal at 773K is continued but in O_2, whereupon the Δ andΨ values return to the pre-annealed values indicating a restoration of the material. Figure 3 shows results from the same experiment, but the real time data over a wide spectral range has been analyzed in terms of the imaginary part of the optical dielectric function, ϵ_2. ϵ_2 is directly related to the optical absorption, so Figure 3 is essentially the absorption spectrum for the YBCOfilm. The before anneal and after O_2 anneal spectra are nearly identical. Tc measured before and after are also good (about 83-85K) but after the vacuum anneal, one sees the large absorption at 4 eV which is an O vacancy charge transfer band in YBCO. There is also a smaller O related band near 2.5 eV. We have used the time dependence of the 4 eV band to determine the O out and in diffusivities during the vacuum and O_2 anneals, respectively. Upon O_2 anneal the 4eV feature disappears and upon re-vacuum anneal it reappears. This experiment demonstrates the ability to study the time evolution of HTSC films in great detail.

Thus, combining the results from this years work with the ToF-ISARS results from last year, the major project objective has been achieved, namely the ability to perform in-situ real time observations on HTSC films using ToF-ISARS and SE. Now with the combined deposition and analysis system nearing completion, we will be able to observe film growth from the nucleation stage onwards in real time.

Development and Application of In-Situ, Real-Time and Ex-Situ Characterization Techniques to Study the Growth of High Temperature Superconducting (HTSC) Films and Interfaces

E.A. Irene Univ. of North Carolina, O. Auciello and G.E. McGuire, MCNC of North Carolina, A.R. Krauss, Argonne Nat'l Laboratory

Technology Issues:
- Thin Film HTSC Devices and Processes
- Detectors; Magnetometers; Memory and Storage Devices

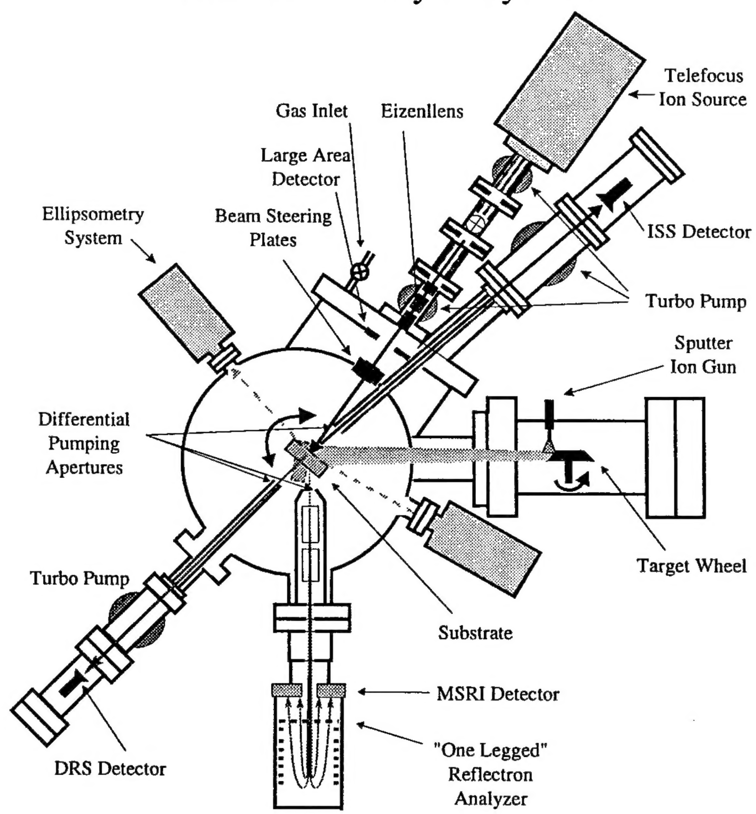
Objectives:
- Demonstrate Time-of-Flight Ion Scattering and Recoil (ToF-ISARS) Spectroscopy and Spectroscopic Ellipsometry (SE) for in-situ and real-time characterization of HTSC thin films and processes.
- Study HTSC thin film processes and interface reactions.

Approach:
- Correlate ToF-ISARS and SE characterization of ion beam deposited 123 HTSC thin films.
- In-situ and real-time analyses as well as ex-situ
- Develop optical models for complex oxides

Accomplishments:
- ToF-ISARS of 123 films after and during deposition
- Correlation of O related adsorption bands in SE with T_c
- Measurement of O in and out diffusion in 123 films using real time SE
- Design and construction of integrated deposition and characterization system

Transitions:
- Coordinating design and construction with small businesses.

TOF-ISARS-SE Ion Beam Deposition and Real-Time Analysis System



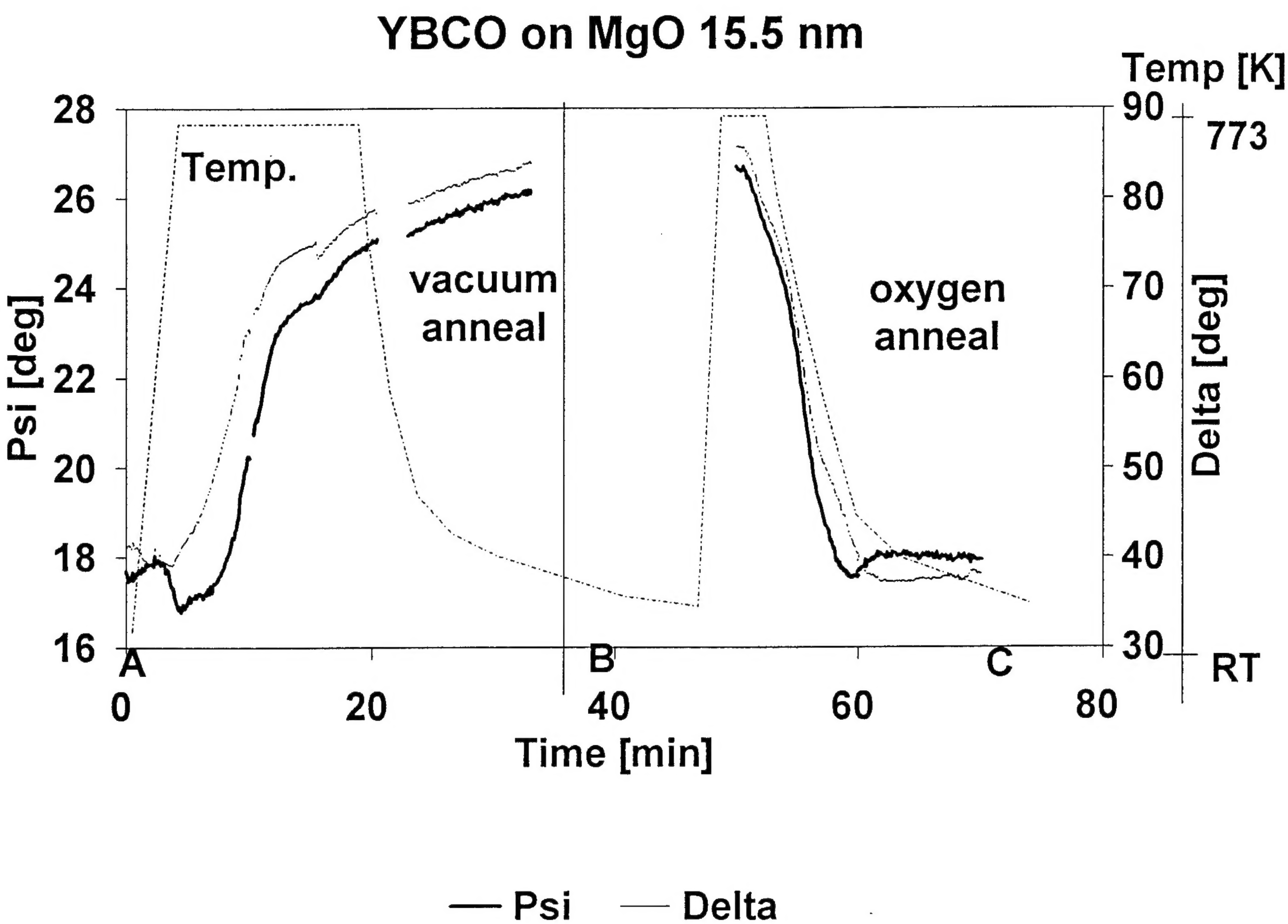


Figure 2 / Irene

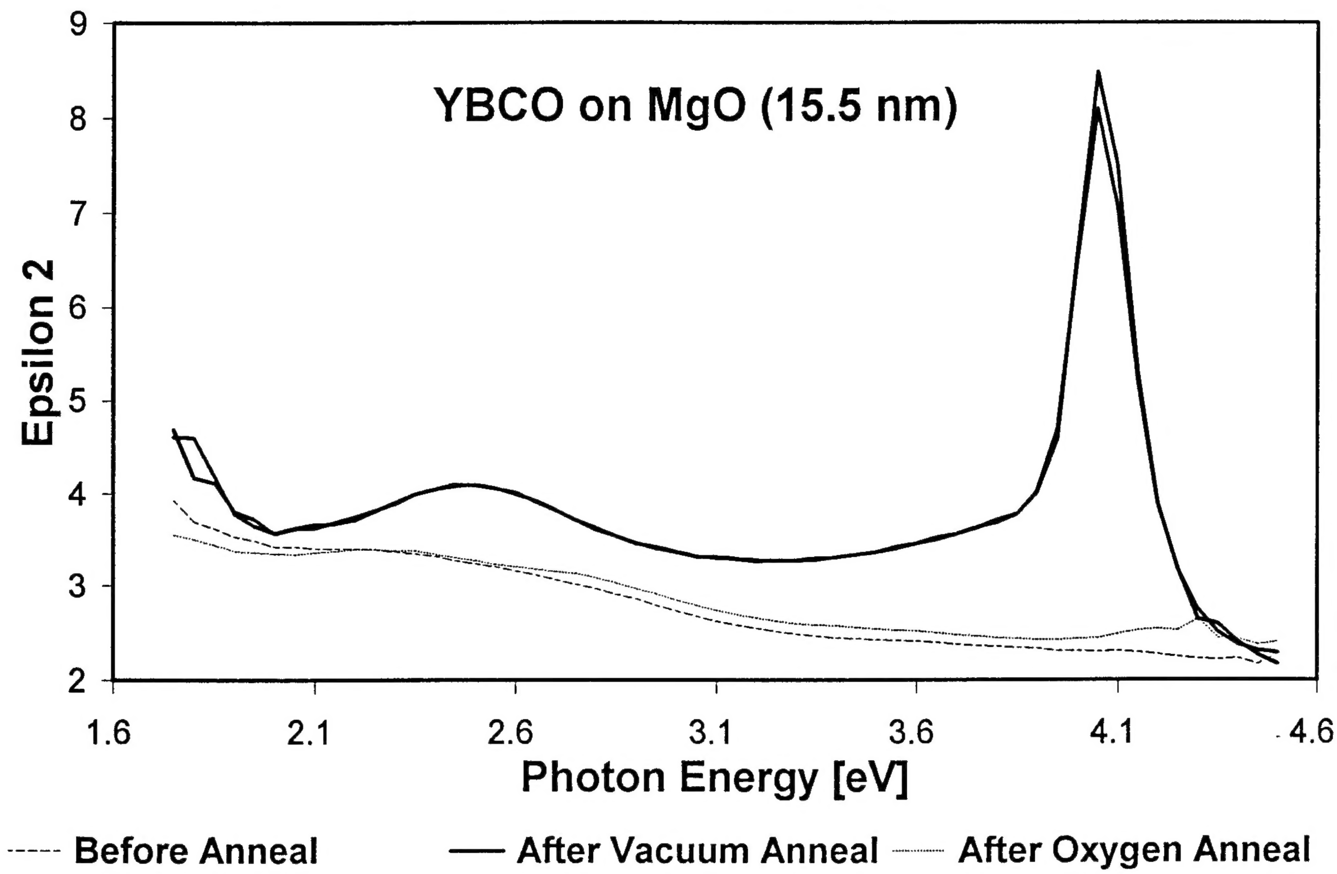


Figure 3 / Irene